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National Performance Audit Program 1980 Proficiency Surveys for Sulfur Dioxide, Nitrogen Dioxide, Carbon Monoxide, Sulfate, Nitrate, Lead and High Volume Flow

(U.S.) Environmental Monitoring Systems Lab.
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Based on authority granted by provisions of the Clean Air Act (42 U.S.C 7410, et seq.), the Quality Assurance Division of the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC administers periodic surveys of analytical proficiency for sulfur dioxide, nitrogen dioxide, carbon monoxide, sulfate, nitrate, lead, and high-volume flow.

Sample materials and devices that have been utilized during the 1980 surveys (performance audits) were developed to simulate collected air pollution samples as faithfully as possible.

Integrity of the various sample materials is continuously monitored to ascertain stability, accuracy, uniformity, and representativeness of the pollutant concentrations.

Since a major survey objective is the assessment of routine analytical performance, a brief evaluative report is promptly returned to each participant. A comprehensive report contains a summary of survey results for the year 1980.

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NATIONAL PERFORMANCE AUDIT PROGRAM

1980 PROFICIENCY SURVEYS

FOR

SULFUR DIOXIDE, NITROGEN DIOXIDE, CARBON MONOXIDE, SULFATE, NITRATE, LEAD AND HIGH VOLUME FLOW

by

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ABSTRACT

Based on authority granted by provisions of the Clean Air Act (42 U.S.C. 7410, et. seq.), the Quality Assurance Division of the Environmental Monitoring Systems Laboratory, Research Triangle Park, N.C. administers periodic surveys of analytical proficiency for sulfur dioxide, nitrogen dioxide, carbon monoxide, sulfate, nitrate, lead, and high-volume flow rate.

The sample materials and devices used for the scheduled surveys (performance audits) have been developed to simulate collected air pollution samples as nearly as possible. Synthetic pollutant samples are prepared in matrices approximating natural air monitoring conditions. Interferents present in real air pollution samples and which influence various analytical methods differently are absent, of course, in artificial samples. The various sample materials are continuously monitored to ascertain stability, accuracy, uniformity, and representativeness of the pollutant concentrations for the respective pollutants.

Since a major objective of the survey is the assessment of routine analytical performance, a brief evaluative report is promptly returned to each participant. A comprehensive report contains a summary of survey results for the year 1980.

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SECTION I
INTRODUCTION

Periodic surveys of analytical proficiency are conducted under the authority of regulations promulgated May 10, 1979 and published in the Code of Federal Regulations, Title 40, Protection of Environment, Part 58, July 1, 1980. This regulation provides for the participation of State or Local Air Monitoring Stations (SLAMS) in EPA's national performance audit program to permit EPA system audits of ambient air monitoring programs.

The 1980 Proficiency Surveys are managed by the Environmental Monitoring Systems Laboratory (EMSL) and are a continuation of regular surveys of analytical proficiency of six ambient air pollutants and high-volume samplers. Sample materials furnished for this purpose are designed to simulate the several types of collected air pollution samples as closely as possible. It is prudent to note that these samples treat only the analytical portion of the total air monitoring capability, and do not deal with errors from sample collection, transportation, handling, storage, and data processing. Rankings in the surveys, except for the few which may result from the occasional unpropitious circumstance, reflect the effectiveness of internal quality assurance programs.

The Proficiency Surveys allow EPA to monitor the caliber of air pollution analyses, and permit the participating agencies to assess their own performances vis-a-vis their peers. With the assistance and cooperation of the EPA Regional Offices, the surveys are conducted by the Quality Assurance Division (QAD)/EMSL, Environmental Research Center, Research Triangle Park, North Carolina 27711. Inquiries and applications to participate should be directed to that address. A discussion of the program, description of the survey materials, statistical summaries and the results are included in this report.

SECTION 2
PROGRAM PROFILE

Participants in the surveys are solicited by the Regional Quality Control Coordinator in each of the ten Regions. Once a laboratory enrolls in a survey for a particular pollutant, it is automatically notified of subsequent surveys of that pollutant. Participants are assigned an identifying code number which remains in effect for all surveys. Included in the surveys are representatives of federal, state, local, industrial and foreign air pollution monitoring agencies.

Soon after a roster is established, instructional information and blind sample materials are transmitted to survey participants. Surveys are presently conducted twice a year for carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), lead (Pb) on filter strips, sulfate ($SO_4^=$) and nitrate (NO_3^-) on filter strips and once a year for high-volume flow. A prompt response includes the reported value and an historical frequency distribution of test results. A comprehensive report is prepared yearly summarizing the survey results of that year.

Laboratories submitting abnormal measurements are offered an opportunity to analyze another set of unknown samples, similar to those of the main survey. However, the retest results are not included in this report.

SECTION 3
STATISTICAL CONSIDERATIONS

Investigators have long agonized over which measurements are totally believable and which are wholly discreditable. Judgment of the investigator was the historical criterion for rejection of data. David Bernoulli, writing in an earlier century about astronomical observations[1], stated that he could see no way of drawing a dividing line between data values that are to be utterly rejected and those that are to be entirely retained. A fair and dispassionate system for judging outliers is needed in any survey.

The criterion chosen for the 1980 surveys is one that has been in use for a long time, the Chauvenet's Criterion.[2] This criterion is based on the normal distribution and advises rejection of an extreme observation if the probability of occurrence of such deviation from the mean of the n measurements is less than 1/2n. Since inclusion of erroneous data vitiates test results by biasing both the survey mean and precison, but removal of valid measurements merely excludes some of the data[3], it is thought that it is better to reject some sound data than to include truly anomalous measurements.

Anomalous values were deleted on the basis of the judgment of survey officials after carefully reviewing overall performance of all participants. Decisions about inclusion of questionable survey data were accomplished on the basis of the objective procedures of Chauvenet's Criterion.

Three of the statistical procedures used to evaluate survey results, the F test, t test and an extension of the analysis of variance, are reviewed below. The F test was used to test whether the variance of one

test method exceeded that of another. The ratio of the variances was not expected to exceed a critical value, which is based on the number of observations (measurements) in each test method, unless differences exist in the precision of the two methods. If F is near one, there is no statistically significant difference in variability between the two methods. Values less than one have no meaning. The value of the statistic F is given by the expression:[4]

$$F = s_1^2/s_2^2 \qquad \text{(Eq. 1)}$$

where:

s_1 = standard deviation of method 1
s_2 = standard deviation of method 2

Two assumptions that underlie the use of the t test for comparing the means of two samples are that their population distributions are normal and that their population variances are equal.[4] When those conditions are satisfied, the variance estimates can be pooled and the statistical relations shown below are assumed to apply. The pooled variance is given by the following equation:

$$s_p^2 \text{ (pooled)} = \frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2} \qquad \text{(Eq. 2)}$$

The standard error of the difference between two means is given by the equation:

$$s_d = \sqrt{\frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2}} \sqrt{\frac{1}{N_1} \quad \frac{1}{N_2}} \qquad \text{(Eq. 3)}$$

The formula for the standard error of the difference between the means is substituted in the formula for t, giving:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{s_p^2}\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} \qquad \text{(Eq. 4)}$$

where:

$\bar{x}_1$ = the average of test method no. 1

$\bar{x}_2$ = the average of test method no. 2

N_1 = no. of measurements by test method no. 1

N_2 = no. of measurements by test method no. 2

To compare the averages of three or more sets of measurements (the t test can compare only two sets), an extension of the analysis of variance[3], the statistic w, is used. If the absolute differences between the averages of all the sets of data are less than w, then it is considered that no statistically significant differences exist among the averages. The critical value of w is computed thus:

$$w = q_{.95} S_e / \sqrt{n} \qquad \text{(Eq. 5)}$$

where:

w = computed critical value from standardized range

$q_{.95}(t,v)$ = a statistic that is a function of the number of data sets, t, and degrees of freedom, v

S_e = pooled standard deviation

$$= \sqrt{\frac{(N_1 - 1)\, S_1^2 + (N_2 - 1)\, S_2^2 + \ldots + (N_t - 1)\, S_t^2}{(N_1 + N_2 + \ldots + N_t) - t}}$$

n = number of data sets

SECTION 4
SURVEY MATERIALS

SULFUR DIOXIDE SAMPLES

The sample material was composed of freeze-dried mixtures of sodium sulfite and potassium tetrachloromercurate (TCM) contained in 5-ml vials. Sample sets consisted of five vials containing 4 to 65 μg of SO_2 equivalent per container. Analyses were performed by the reference method for the determination of SO_2 in the atmosphere (pararosaniline method).[5] The sample forms a dichlorosulfitomercurate complex when solubilized in 0.04N TCM. This complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methylsulfonic acid. The absorbance of the solution is measured spectrophotometrically at 548 nm.

Representative samples from each concentration level were analyzed (Table 1) and the analyzed values are the reference values of surveys 0480 and 1080 (surveys are numbered by month and year). Independent corroborative tests were conducted by another laboratory. The presumption was that each sample was collected in 50 mL of absorbing reagent with a total sample air volume of 30OL.

NITROGEN DIOXIDE SAMPLES

The samples consisted of 20 mL of aqueous sodium nitrite contained in glass ampoules. A set consisted of 5 ampoules. The samples simulated ambient samples ranging in concentration from 0.15 to 1.5 μg/mL when mixed with caustic absorbing reagent.

Analyses were performed using an equivalent method for the determination of NO_2 in ambient air.[6] Measurements were made spectrophotometrically at 540 nm. The values contained in Table 2 are the reference values for surveys 0680 and 1280. Values are based on 5 mL of the sample being diluted to 50 mL with absorbing reagent.

TABLE 1. CONCENTRATIONS OF SULFUR DIOXIDE SURVEY SAMPLES

Survey 0480 μg SO_2/m^3			Survey 1080 μg SO_2/m^3		
Sample no.	Reference value	Expected range (±2s)	Sample no.	Reference value	Expected range (±2s)
1	13.2	10.5 to 15.9	1	23.2	13.5 to 32.9
2	45.7	34.8 to 56.6	2	53.9	49.1 to 58.7
3	94.0	91.8 to 96.2	3	73.1	65.2 to 81.0
4	144.3	126.3 to 162.3	4	145.9	139.2 to 152.6
5	216.0	208.6 to 223.4	5	205.2	195.2 to 215.2

TABLE 2. CONCENTRATIONS OF NITROGEN DIOXIDE SURVEY SAMPLES

Survey 0680 μg/mL NO_2			Survey 1280 μg/mL NO_2		
Sample no.	Reference value	Expected range (±2s)	Sample no.	Reference value	Expected range (±2s)
1	0.350	0.330 to 0.370	1	0.147	0.139 to 0.155
2	0.449	0.445 to 0.453	2	0.396	0.390 to 0.402
3	0.691	0.685 to 0.697	3	0.741	0.735 to 0.747
4	0.941	0.937 to 0.945	4	1.230	1.222 to 1.238
5	1.140	1.134 to 1.146	5	1.475	1.466 to 1.484

CARBON MONOXIDE SAMPLES

Samples consisted of compressed gas mixtures of carbon monoxide (CO) and artificial air along with 2 ppm of methane (CH_4) and approximately 365 ppm of carbon dioxide (CO_2). Aluminum cylinders were used in the surveys. Sample concentrations ranged from 8 to 43 ppm of CO. Each participant received a set of three cylinders, one from each of three concentration levels.

Verification testing was accomplished by non-dispersive infrared analysis. Representative samples from each concentration level were analyzed by QAD and an independent testing laboratory. The reference values for surveys 0380 and 0980 are listed in Table 3.

TABLE 3. CONCENTRATIONS OF CARBON MONOXIDE SURVEY SAMPLES

Survey 0380			Survey 0980		
ppm CO			ppm CO		
Sample no.	Reference value	Expected range (±2s)	Sample no.	Reference value	Expected range (±2s)
1	8.24	8.16 to 8.32	1	10.5	10.4 to 10.6
2	26.8	26.7 to 26.9	2	21.1	20.3 to 21.9
3	43.3	43.2 to 43.4	3	39.7	39.5 to 39.9

SULFATE-NITRATE SAMPLES

Samples consisted of 1.9 x 20 cm (0.75 x 8 in.) glass fiber filter strips with depositions of potassium sulfate (K_2SO_4) and lead nitrate ($Pb[NO_3]_2$). Filter strip samples included concentrations of various SO_4

and NO_3 concentrations. Each strip was sealed in a plastic envelope. The concentrations of sulfate ranged from approximately 1.2 to 32 $\mu g/m^3$. Nitrate levels spanned between 0.6 and 14 $\mu g/m^3$. Concentrations were determined using the requisite filter dimensions of 20 x 25.4 cm (8 x 10 in) and a collected air volume of 2000 m^3. Presuming that gravimetric preparation and transfer onto the filter strips could be carried out more accurately than could existing analytical methods, the reference values were obtained theoretically from the deduced mass of inorganic salts deposited on the filters. Verification by ion chromatographic analyses assured that the accuracy and precision of the samples were within prescribed limits. The sulfate concentrations are given in Table 4 and the nitrate values are listed in Table 5. These were the values which were applied to surveys 0280 and 0880.

TABLE 4. CONCENTRATIONS OF SULFATE SURVEY SAMPLES

Survey 0280			Survey 0880		
Sample no.	$\mu g\ SO_4^{=}/m^3$/filter		Sample no.	$\mu g\ SO_4^{=}/m^3$/filter	
	Reference value	Expected range (±2s)		Reference value	Expected range (±2s)
0	25.20	24.67 to 25.73	0	11.80	10.96 to 12.64
1	7.50	6.34 to 8.66	1	22.00	21.86 to 22.14
2	1.20	0.95 to 1.45	2	1.60	1.55 to 1.65
3	12.00	11.79 to 12.21	3	6.80	6.31 to 7.29
4	18.00	17.56 to 18.44	4	17.00	15.91 to 18.09
5	32.40	31.77 to 33.03	5	27.20	25.43 to 28.97

TABLE 5. CONCENTRATIONS OF NITRATE SURVEY SAMPLES

Survey 0280			Survey 0880		
Sample no.	$\mu g\ NO_3^-/m^3$/filter		Sample no.	$\mu g\ NO_3^-/m^3$/filter	
	Reference value	Expected range (±2s)		Reference value	Expected range (±2s)
0	9.90	9.64 to 10.16	0	6.00	5.59 to 6.44
1	2.40	2.05 to 2.75	1	11.40	11.07 to 11.73
2	4.20	4.08 to 4.32	2	0.60	0.54 to 0.66
3	6.00	5.90 to 6.10	3	3.30	3.04 to 3.56
4	7.80	7.57 to 8.03	4	8.70	8.17 to 9.23
5	0.80	0.64 to 0.96	5	14.10	13.19 to 15.01

LEAD SAMPLES

Samples were composed of 1.9 x 20 cm (0.75 by 8 in) glass fiber filter strips with depositions of lead nitrate ($Pb[NO_3]_2$). Filter strip sample sets contained combinations of various lead concentrations, each sealed in a plastic envelope. The lead content ranged from 0.6 to 9.9 $\mu g/m^3$. Concentrations were calculated presuming that the samples were collected on the prescribed 20 x 25.4 cm (8 x 10 in) hi-vol filter with a total air volume of 2000 m^3.

The precision and accuracy measurements of this sample material were accomplished by atomic absorption analysis. The reference values used in surveys 0180 and 0780 are listed in Table 6.

TABLE 6. CONCENTRATIONS OF LEAD SURVEY SAMPLES

Survey 0180			Survey 0780		
	μg Pb/m^3/filter			μg Pb/m^3/filter	
Sample no.	Reference value	Expected range (± 2s)	Sample no.	Reference value	Expected range (± 2s)
0	9.90	9.67 to 10.13	0	0.60	0.59 to 0.60
1	6.30	6.13 to 6.47	1	6.60	6.38 to 6.82
2	8.10	7.92 to 8.28	2	1.80	1.75 to 1.85
3	4.50	4.43 to 4.57	3	5.40	5.25 to 5.55
4	2.70	2.63 to 2.76	4	3.00	2.90 to 3.10
5	0.90	0.89 to 0.91	5	4.20	4.10 to 4.30

HIGH VOLUME REFERENCE FLOW DEVICE (ReF)

A single ReF was supplied to each participating agency. Organizations were instructed to check as many hi-vol sampling units as feasible within the allotted time. The unit received by each laboratory consisted of a modified orifice, wind deflector and manometer. Resistance plates simulated particulate loading of a high volume filter.

The ReF was mounted on top of the sampler replacing the filter face plate during measurement of the air flow of a hi-vol sampler, as shown in Figure 1. A wind deflector was necessary to prevent fluctuation in the readings due to wind blowing across the orifice. The resistance plates, when inserted into the ReF, simulated various filter loading conditions, as illustrated in Figure 2.

By calibrating each ReF with a positive displacement meter (Roots meter), in conjunction with measurements of pressure drops and temperatures, a calibration curve in the form of an orifice equation was derived.

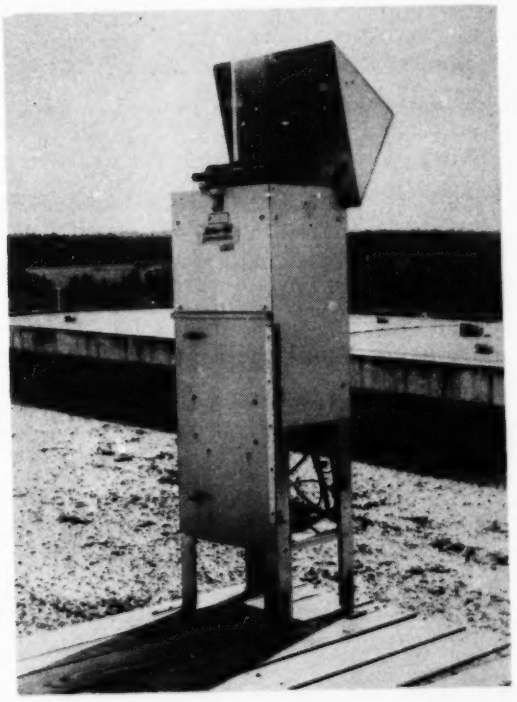


Figure 1. Reference flow device mounted on high volume sampler.

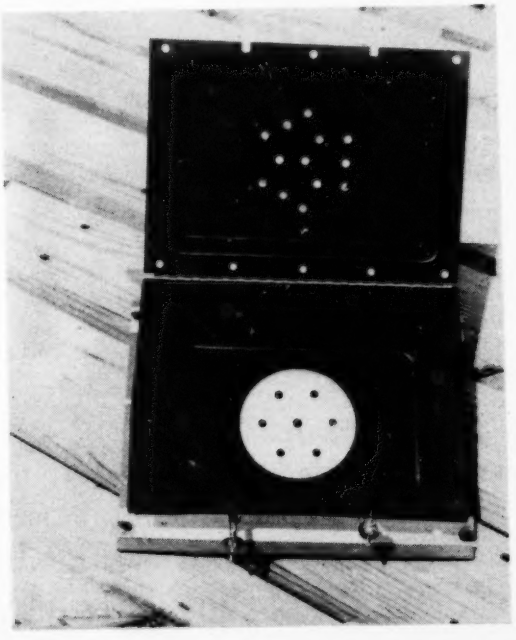


Figure 2. Reference flow device with resistance plate.

The equation shown below was used to determine the "K" orifice constant for each unit.

$$Q_1 = AYC \sqrt{\frac{\Delta P \; T_1}{P_1}} \qquad \text{(Eq. 6)}$$

where:

Q_1 = volumetric flow at conditions of T_1 and P_1 (m^3/min)
A = area of orifice (in^2)
Y = expansion factor
C = orifice coefficient
ΔP = pressure drop across orifice (in H_2O)
P_1 = upstream pressure (barometric pressure,mm Hg)
T_1 = upstream temperature (ambient temperature, °K)

Because A is constant for a given orifice, and Y and C are essentially constant over the flow range in question, a new orifice constant "K" was defined as:

$$K = AYC \qquad \text{(Eq. 7)}$$

Thus, the orifice equation becomes:

$$Q_1 = K \sqrt{\frac{\Delta P \; T_1}{P_1}} \qquad \text{(Eq. 8)}$$

During calibration of the ReF, Q_1, ΔP, T_1 and P_1 were also measured. The constant K was determined by regressing a series of Q_1 measurements onto the square root of the values under the radical. During the survey, operating personnel measured ΔP, T_1 and P_1. By knowing K, the "true flow" can be calculated. This flow was compared with the flow measured by the high volume sensor to determine the accuracy of flow measurements.

SECTION 5
RESULTS

SULFUR DIOXIDE

Test Methods

Approximately 76 percent of the respondents in 0480 and 1080 surveys used the manual procedure, and 24 percent the automated pararosaniline procedures. The statistical t test, computed for the differences between the averages of the results of the two survey test methods, indicated no significance. The F test was employed to evaluate whether the variability of one of the methods exceeded that of the other. It was clear that the manual method exhibited substantially greater survey variability.

Agency Apportionment

Participation in both the April, 1980 and October, 1980 surveys declined from the previous year. The reduction was distributed among all categories of agencies and was accounted for by decreased use of the pararosaniline test method. The distribution of agencies in the surveys is shown in Table 7.

TABLE 7. AGENCY APPORTIONMENT OF SULFUR DIOXIDE SURVEYS

Agency	Survey 0480, %	Survey 1080, %
State	38	36
Local	44	45
Industrial/Contractor	17	18
Foreign	1	1

Data Summary

Survey results of all methods are summarized in Table 8. Results according to analytical method are given in Table 9. The frequency distribution of the results in terms of percent of reference values is given in Table 10. The reference values are the best estimates of the true concentrations and are derived from the analyses performed by EPA laboratories, a commercial corroborative laboratory (Stewart Laboratories, Inc.), and the manufacturer's laboratories (Northrop Services, Inc.). The sample materials were evaluated for stability, homogeneity, and accuracy before use in the survey.

TABLE 8. SUMMARY OF SULFUR DIOXIDE PROFICIENCY SURVEYS

Sample no.	Respondents*	Reference value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0480 (April 1980)					
1	86	13.20	12.26	6.85	1.10 - 33.33
2	90	45.70	42.40	8.25	15.72 - 60.40
3	90	94.00	86.04	13.32	44.40 - 121.42
4	87	144.00	136.15	26.04	56.72 - 197.14
5	90	216.00	218.85	25.38	156.80 - 292.85
Survey 1080 (October 1980)					
1	71	23.2	23.63	6.40	7.45 - 41.07
2	71	53.9	52.09	7.13	36.63 - 65.00
3	71	73.1	69.60	7.57	52.27 - 86.70
4	73	145.9	139.78	11.49	108.00 - 172.41
5	73	205.2	197.10	19.45	138.90 - 242.79

*With outliers removed.

TABLE 9. SULFUR DIOXIDE BY ANALYTICAL METHOD

($\mu g/m^3$)

Survey 0480* (April 1980)

Sample no.	Pararosaniline - manual			Pararosaniline - automated		
	N†	Mean	Std. dev.	N	Mean	Std. dev.
1	71	11.90	8.63	21	12.16	5.67
2	71	43.74	11.66	21	42.44	7.20
3	71	88.47	19.20	22	86.77	8.41
4	71	134.65	39.10	21	124.30	41.56
5	70	222.07	41.57	22	213.13	22.17

Survey 1080* (October 1980)

Sample no.	Pararosaniline-manual			Pararosaniline-automated		
	N	Mean	Std. dev.	N	Mean	Std. dev.
1	58	23.52	7.99	15	24.47	5.45
2	56	51.77	7.54	16	54.61	7.52
3	58	69.00	9.15	15	72.19	8.16
4	59	139.44	15.22	16	141.57	13.07
5	59	195.95	24.71	16	199.46	19.61

*Outliers removed.
†Number of respondents.

TABLE 10. PERCENT OF SULFUR DIOXIDE MEASUREMENTS WITHIN INDICATED PERCENT OF REFERENCE VALUE

Survey 0480						Survey 1080					
Sample no.	Value	10%	20%	30%	50%	Sample no.	Value	10%	20%	30%	50%
1	13.2	12.1	26.4	46.2	57.1	1	23.25	30.8	52.6	69.2	84.6
2	45.7	52.1	71.9	82.3	91.7	2	53.92	47.4	79.5	88.5	93.6
3	94.0	50.0	71.9	89.6	95.8	3	73.12	55.7	83.5	91.1	94.9
4	144.0	47.9	74.5	81.9	91.5	4	145.9	66.7	87.7	92.6	97.5
5	216.0	69.8	82.3	92.7	97.9	5	205.2	71.6	84.0	92.6	96.3

The mean values from sulfur dioxide survey 0480, plotted against the reference values, gave a linear relationship, as follows:

$$y = a + bx \qquad \text{(Eq. 7)}$$

where:

y = survey average

x = reference value

a = y intercept = -4.7803

b = slope = 1.0131

R^2= coefficient of linearity squared = 0.9969

y = -4.7803 + 1.0131 (reference value)

The plot of the survey means (y) against the reference values (x) is shown in Figure 3.

The means for survey 1080, plotted against the reference values, gave a linear relationship, as follows:

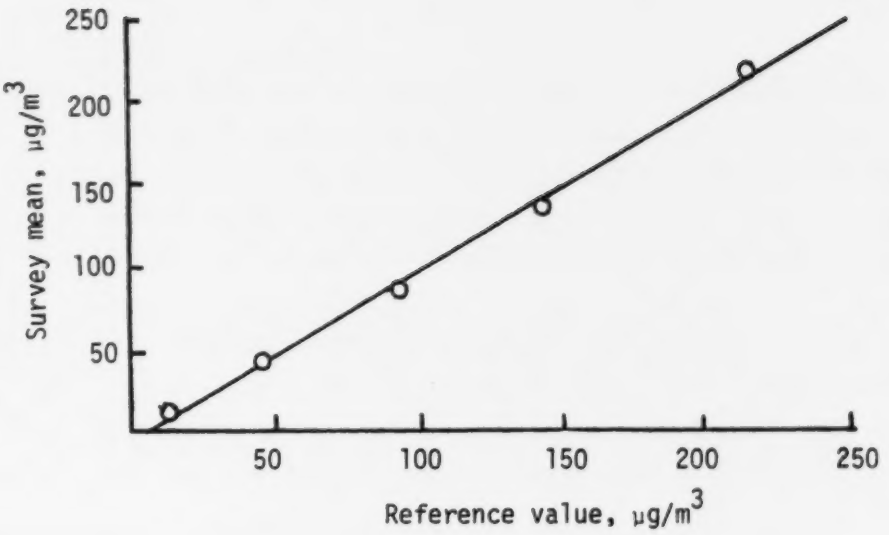
Survey average = 0.6377 + 0.9554 (reference value)

R^2 = 0.9999

The plot of the survey means (y) against the reference values (x) is shown in Figure 4.

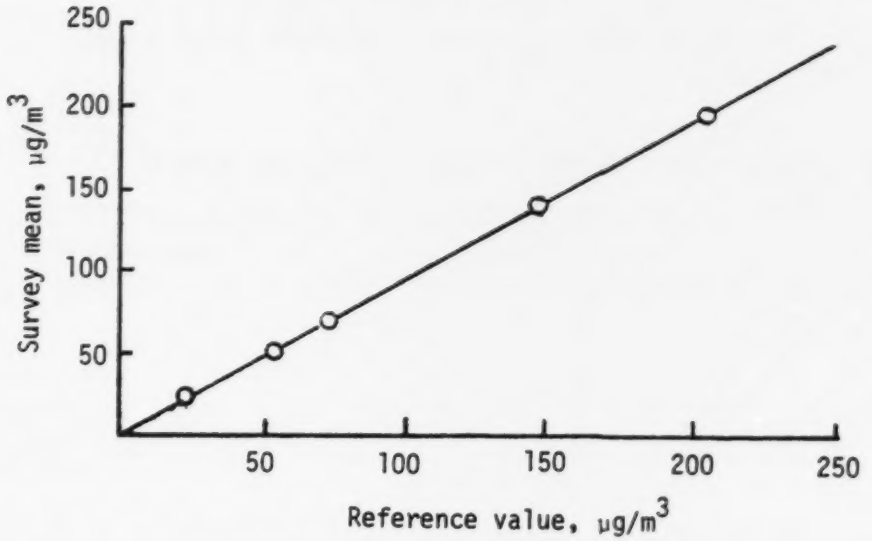
Resume

Proficiency surveys for SO_2 were conducted in April and October, 1980. Seventy-one laboratories completed the 0480 survey, 13 fewer than the 1080 test. The pararosaniline method predominated with about 75 percent of the laboratories using that procedure. No systematic discrepancies or substantial bias were found in the SO_2 surveys.



x	y
13.20	12.26
42.70	42.40
94.00	86.04
144.00	136.15
216.00	218.85

Figure 3. Means of SO_2 survey 0480 vs. reference values.



x	y
23.25	23.63
53.92	52.09
73.12	69.60
145.90	139.78
205.20	197.10

Figure 4. Mean values of SO_2 survey 1080 vs. reference values.

NITROGEN DIOXIDE

Test Methods

The manual sodium arsenite colorimetric procedure was used by 68 percent of the respondents in both the 0680 and 1280 surveys. Around 22 percent of respondents used the automated sodium arsenite method. The manual Saltzman and TGS-ANSA manual methods made up the balance of the test methods. Several participants did not indicate the method of analysis.

According to the statistical t test, differences between the means of the predominant test methods were without significance. Variability between the two major methodologies was measured by the F test. Equivocal results indicated that neither method was without merit.

Agency Apportionment

Participation in the 1980 Proficiency Survey decreased by 17 percent from the 1979 level[7], with the second of the twice yearly tests having approximately 12 percent fewer laboratories taking part. The agency categories included in the NO_2 surveys are shown in Table 11.

TABLE 11. AGENCY APPORTIONMENT OF NITROGEN DIOXIDE SURVEYS

Agency	Survey 0680, %	Survey 1280, %
State	37	35
Local	50	52
Industrial/Contractor	12	12
Foreign	1	1

Data Summary

Survey results of all methods are tabulated in Table 12. Table 13 lists the results by specific analytical method. Frequency distributions by percent of the reference value are shown in Table 14. This table shows the percentages of reported measurements which lie within the indicated percent (10, 20, 30, or 50) of the reference value. The reference values, or best estimates of the true concentrations, were derived from analyses performed by the QAD, by a commercial testing laboratory (Stewart Laboratories, Inc.) and by the manufacturer (Northrop Services, Inc). The sample material was tested for conformity to established criteria for precision and accuracy.

TABLE 12. SUMMARY OF NITROGEN DIOXIDE PROFICIENCY SURVEYS

Sample no.	Respondents*	Reference value µg/mL	Survey mean µg/mL	Survey std. dev. µg/mL	Survey interval µg/mL
Survey 0680 (June 1980)					
1	72	0.350	0.346	0.020	0.300 - 0.424
2	72	0.449	0.440	0.020	0.362 - 0.494
3	73	0.691	0.683	0.031	0.584 - 0.760
4	73	0.941	0.928	0.046	0.772 - 1.072
5	73	1.140	1.118	0.049	0.990 - 1.210
Survey 1280 (December 1980)					
1	64	0.147	0.152	0.010	0.122 - 0.179
2	63	0.396	0.407	0.015	0.365 - 0.433
3	65	0.741	0.759	0.026	0.689 - 0.820
4	63	1.230	1.256	0.045	1.146 - 1.375
5	64	1.475	1.508	0.049	1.353 - 1.600

*With outliers removed.

TABLE 13. NITROGEN DIOXIDE BY ANALYTICAL METHOD
µg/mL

	Saltzman-manual			Sodium arsenite-manual			Sodium arsenite-automated			TGS-ANSA manual		
Sample no.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
Survey 0680* (June 1980)												
1	3	0.241	0.110	52	0.344	0.015	18	0.336	0.046	1	0.343	0.000
2	4	0.378	0.064	52	0.441	0.017	16	0.434	0.030	1	0.442	0.000
3	4	0.632	0.065	52	0.690	0.043	16	0.680	0.037	1	0.699	0.000
4	4	0.803	0.102	52	0.933	0.037	16	0.915	0.056	1	0.959	0.000
5	4	1.050	0.077	52	1.115	0.061	16	1.115	0.060	1	1.144	0.000
Survey 1280* (December 1980)												
1	2	0.160	0.012	44	0.152	0.011	13	0.149	0.007	2	0.151	0.013
2	2	0.415	0.011	45	0.407	0.014	11	0.405	0.018	2	0.396	0.009
3	2	0.769	0.005	45	0.760	0.026	13	0.754	0.038	2	0.766	0.006
4	2	1.251	0.054	44	1.261	0.053	12	1.235	0.034	2	1.253	0.009
5	2	1.530	0.049	45	1.506	0.061	13	1.477	0.083	2	1.532	0.025

*With outliers removed.

TABLE 14. PERCENT OF NITROGEN DIOXIDE MEASUREMENTS WITHIN INDICATED PERCENT OF REFERENCE VALUE

Survey 0680						Survey 1280					
Sample no.	Reference value	10%	20%	30%	50%	Sample no.	Reference value	10%	20%	30%	50%
1	0.350	84.2	93.4	94.7	98.7	1	0.147	81.7	91.5	91.5	94.4
2	0.449	88.3	93.5	98.7	98.7	2	0.396	88.7	90.1	91.5	93.0
3	0.691	88.3	96.1	97.4	98.7	3	0.741	91.4	94.3	95.7	97.1
4	0.941	89.6	96.1	98.7	98.7	4	1.230	88.6	91.4	92.9	94.3
5	1.140	88.3	96.1	98.7	98.7	5	1.475	88.9	91.7	93.1	94.4

The means from nitrogen dioxide survey 0680, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 0.00237 + 0.98101 (reference value)
$R^2 = 0.9999$

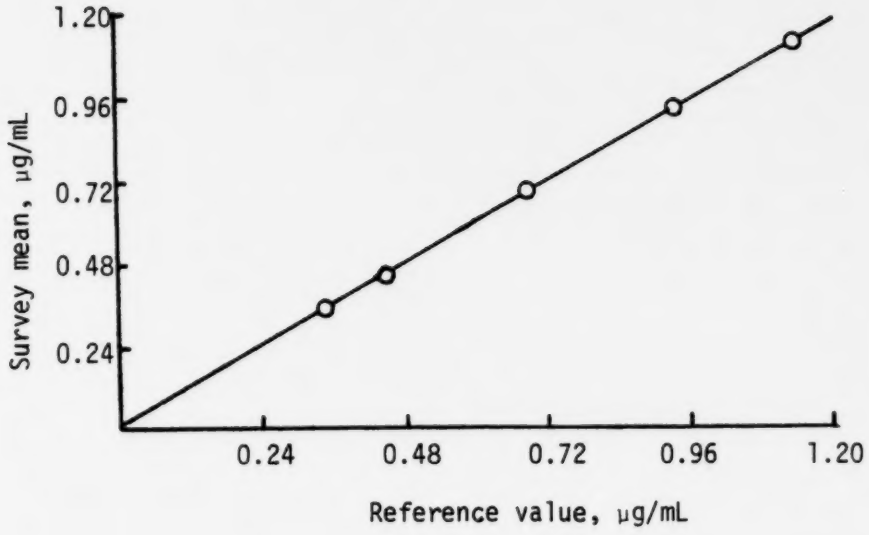
The plot of the survey means (y) against the reference values (x) is shown in Figure 5. The means from survey 1280, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 0.00250 + 1.0202 (reference value)
$R^2 = 1.0000$

The plot of the survey means (y) against the reference values (x) is shown in Figure 6.

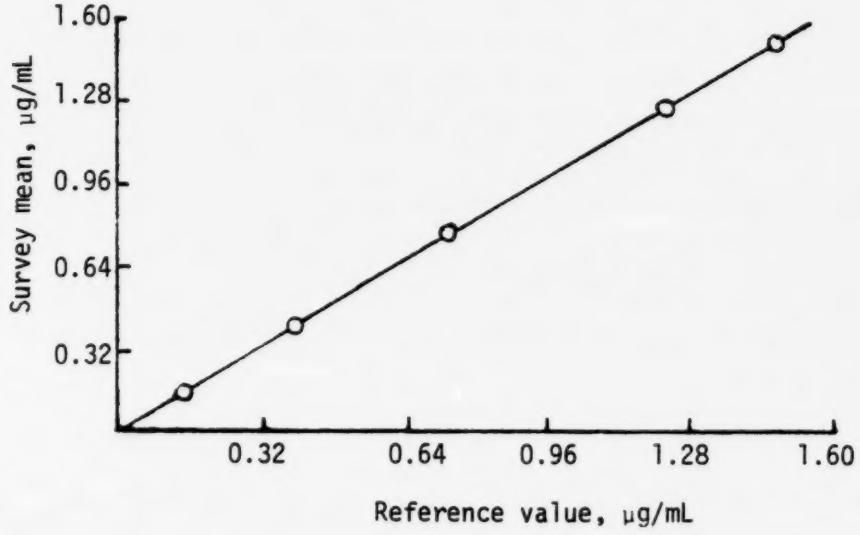
Resume

NO_2 Proficiency Surveys were conducted in June and December 1980 with 73 laboratories participating in the summer survey and 65 in the winter test. The analytical method used by approximately 68 percent of the respondents was the manual sodium arsenite procedure. No systematic discrepancies or substantial bias were evident in the NO_2 survey data.



x	y
0.350	0.346
0.449	0.440
0.691	0.683
0.941	0.928
1.140	1.118

Figure 5. Mean values of NO_2 survey 0680 vs. reference values.



x	y
0.147	0.152
0.396	0.407
0.741	0.759
1.230	1.256
1.475	1.508

Figure 6. Mean values of NO_2 survey 1280 vs. reference values.

CARBON MONOXIDE

Test Methods

The NDIR method dominated, with approximately 95 percent of the laboratories using that method in both the March and September tests. The GC method accounted for the remainder of the test results.

Application of the t test determined that differences between the averages of the two analytical methods were of statistical significance in sample levels 1 and 2 of the March, 1980 survey and in sample 2 of the September, 1980 test. In survey 0380, use of the F test verified that, on the whole, the GC method exhibited greater survey variability; results of the 0980 survey were generally the same. The great disparity in the number of laboratories using the two methods confounded comparison of the results. Were the number of users of the GC method closer to the number using the NDIR method, conclusions concerning relative variability could have been more decisive.

Agency Apportionment

Laboratories taking part in the 1980 CO Proficiency Surveys numbered close to those participating during the previous year[7]. State and local participation changed little from the 1979 level. The agencies comprising the 1980 CO surveys are shown in Table 15.

Data Summary

The results of all methods used in the 1980 CO surveys are summarized in Table 16. The results arranged by analytical test method, are shown in Table 17. The percentiles of reported measurements which were within the indicated percent (10, 20, 30 and 50) of the reference value are presented in Table 18. The reference values were assigned after considering results of the analyses by the QAD, Stewart Laboratories, Inc., and the manufacturer of the samples, Airco Industrial Gases.

TABLE 15. AGENCY APPORTIONMENT OF CARBON MONOXIDE SURVEYS

Agency	Survey 0380, %	Survey 0980, %
Federal	2	2
State	51	48
Local	40	43
Industrial/Contractor	6	6
Foreign	1	1

TABLE 16. SUMMARY OF CARBON MONOXIDE PROFICIENCY SURVEYS

Sample No.	Respondents*	Reference value ppm	Survey mean ppm	Survey std. dev. ppm	Survey interval ppm
Survey 0380 (March 1980)					
1	334	8.24	8.05	0.58	5.40 - 10.2
2	339	26.8	26.64	1.11	22.3 - 30.7
3	325	43.3	43.22	1.73	37.75 - 48.0
Survey 0980 (September 1980)					
1	309	10.5	10.40	0.58	8.00 - 12.5
2	299	21.1	21.28	0.91	18.2 - 24.5
3	293	39.7	39.64	1.36	34.2 - 44.1

*With outliers removed.

TABLE 17. CARBON MONOXIDE BY ANALYTICAL METHOD
(ppm)

Sample No.	NDIR N	NDIR Mean	NDIR Std. dev.	GC N	GC Mean	GC Std. dev.
Survey 0380* (March 1980)						
1	321	8.00	0.70	16	7.02	1.88
2	322	26.64	1.22	16	25.89	2.81
3	308	43.22	2.01	16	42.49	1.58
Survey 0980* (September 1980)						
1	292	10.39	0.58	17	10.53	0.69
2	283	21.31	0.99	17	20.37	2.74
3	278	39.66	1.72	17	39.75	1.03

*Outliers removed.

TABLE 18. PERCENT OF CARBON MONOXIDE MEASUREMENTS WITHIN INDICATED PERCENT OF REFERENCE VALUE

Survey 0380						Survey 0980					
Sample no.	Expected value	10%	20%	30%	50%	Sample no.	Expected value	10%	20%	30%	50%
1	8.24	85.6	97.1	99.4	100.0	1	10.5	88.0	97.5	100.0	100.0
2	26.8	94.8	100.0	100.0	100.0	2	21.1	90.2	94.6	98.7	100.0
3	43.3	96.4	100.0	100.0	100.0	3	39.7	94.2	97.1	100.0	100.0

The mean values from survey 0380, plotted against the reference values, gave a linear relationship, as follows:

Survey average = -0.2642 + 1.0059 (reference value)

$R^2 = 1.0000$

The plot of the survey means (y) against the reference values (x) is shown in Figure 7.

The means from survey 0980, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 0.0126 + 0.9997 (reference value)
$R^2 = 0.9999$

A plot of the survey mean (y) against the reference values (x) is shown in Figure 8.

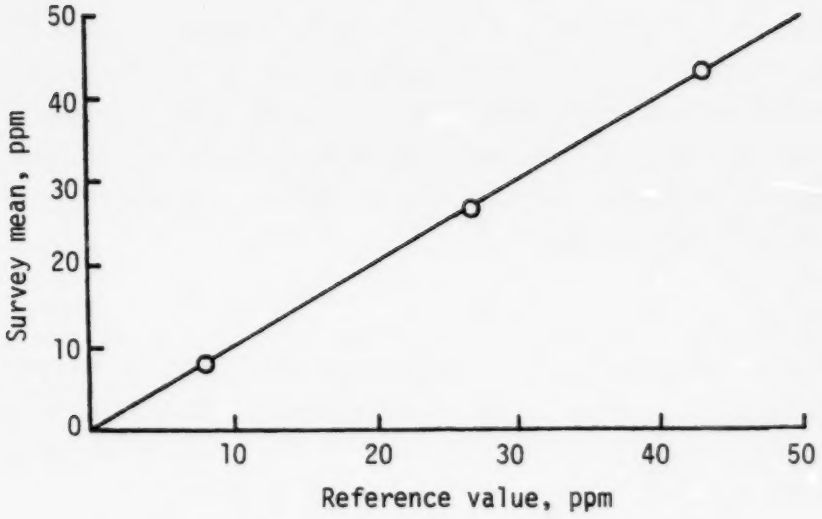
Resume

Proficiency Surveys for CO were conducted in March and September 1980. Operational assessment of approximately 300 instruments was included in each of the semiannual surveys. The NDIR method was employed by approximately 95 percent of the survey respondents. The precision of the NDIR method proved to be generally superior to that of the GC procedure.

SULFATE

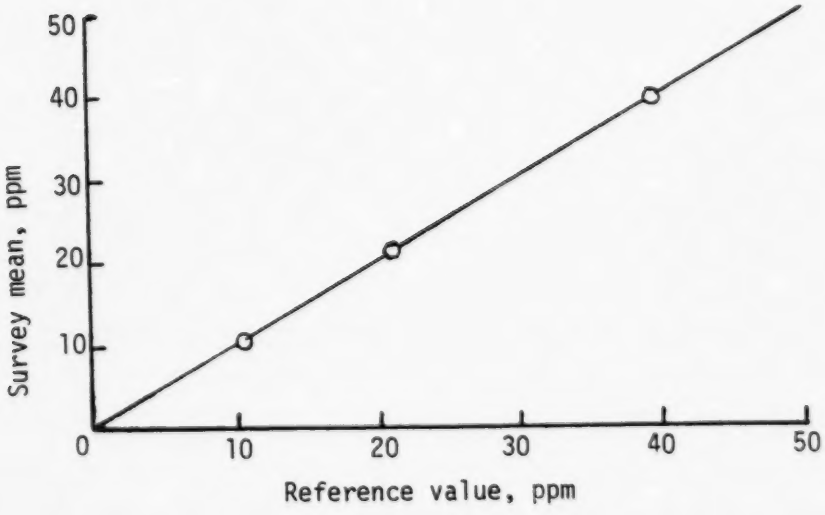
Test Method

Participants in the 0280 and 0880 surveys employed four principal test methods: the automated methylthymol blue, manual barium chloride, manual Sulfa-Ver© and ion chromatographic procedures. The relative use of the methods changed little between the semiannual tests, approximately 40 percent used the methylthymol blue, 30 percent the manual barium chloride, 15 percent the Sulfa-Ver© methods and 15 percent the sensitive and accurate ion chromatographic method. The remainder used other methods or else the methodology was unspecified.



x	y
8.24	8.05
26.80	26.64
43.30	43.22

Figure 7. Mean values of CO survey 0380 vs. reference values.



x	y
10.50	10.40
21.10	21.28
39.70	39.64

Figure 8. Mean values of CO survey 0980 vs. reference values.

The averages of all the named test methods were compared at the 5 percent significance level by an extension of the analysis of variance. The absolute differences between the means of the separate methods exceeded the critical value of w in level 5 of survey 0880, indicating that the averages differed. Further statistical analysis of that level showed that the manual Sulfa-Ver® method contributed the difference. The averages of the other tested methods at this level were not statistically distinguishable. The averages of the major methods did not differ statistically in the balance of the two 1980 surveys.

Agency Apportionment

Agency balance in the 1980 surveys differed little from the distribution during the previous survey period.[7] As expected, state and local agencies composed the greater part of the roster. The classification of agencies involved in the 1980 surveys is shown in Table 19.

TABLE 19. AGENCY APPORTIONMENT OF SULFATE SURVEYS

Agency	Survey 0280, %	Survey 0880, %
Federal	2	2
State	47	42
Local	26	29
Industrial/Contractor	18	20
Foreign	7	7

Data Summary

The survey results of all methods are tabulated in Table 20. Results listed by analytical method are shown in Table 21. Frequency distributions of the percent of measurements falling within the indicated percent of the reference value are presented in Table 22. The reference values used

in the sulfate surveys were the theoretical concentration of sulfate ion of an inorganic salt which was deposited on glass fiber filter strips. The theoretical values were confirmed by corroborative analyses by the QAD, Northrop Services, Inc. and Stewart Laboratories, Inc.

TABLE 20. SUMMARY OF SULFATE PROFICIENCY SURVEYS

Sample no.	Respondents	Reference value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0280 (February 1980)					
0	54	25.20	23.24	1.74	17.00 - 26.70
1	54	7.50	7.50	1.72	0.56 - 14.60
2	51	1.20	1.81	0.97	0.21 - 4.80
3	54	12.00	11.45	1.00	9.22 - 13.50
4	53	18.00	16.58	2.67	7.12 - 20.30
5	55	32.40	28.45	3.33	17.46 - 37.44
Survey 0880 (August 1980)					
0	54	11.80	11.72	1.36	8.45 - 17.55
1	60	22.00	21.49	2.37	11.70 - 30.00
2	55	1.60	2.92	3.31	0.31 - 15.25
3	56	6.80	6.52	1.30	0.62 - 9.18
4	59	17.00	17.21	2.58	11.90 - 25.00
5	60	27.20	26.27	2.29	19.50 - 31.45

*With outliers removed.

TABLE 21. SULFATE BY ANALYTICAL METHOD
($\mu g/m^3$)

Survey 0280* (February 1980)

	Methylthymol blue-automated			Barium chloride-manual			Barium chloride-automated			Sulfa-Ver-manual			Ion chromatograph		
Sample no.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
0	20	23.25	1.18	17	23.08	2.81	1	24.00	0.00	10	22.37	3.92	9	23.58	1.72
1	20	7.99	2.57	17	8.03	3.81	1	9.96	0.00	10	7.12	1.22	8	7.23	0.71
2	20	1.67	0.89	15	2.15	1.73	1	1.87	0.00	10	2.12	1.28	9	1.29	0.18
3	20	11.66	0.68	16	11.50	1.58	1	10.67	0.00	10	11.18	1.04	8	11.66	0.74
4	20	16.79	4.88	16	15.86	3.70	1	16.13	0.00	10	16.16	2.05	8	17.77	0.76
5	20	28.16	3.06	17	26.30	6.90	1	29.11	0.00	10	28.74	4.82	8	30.08	1.20

Survey 0880* (August 1980)

	Methylthymol blue-manual			Methylthymol blue-automated			Barium chloride-manual			Barium chloride-automated			Sulfa-Ver-manual			Ion chromatograph		
Sample no.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
0	1	11.50	0.00	23	10.68	2.63	16	11.59	3.11	1	12.15	0.00	8	10.79	3.29	9	11.47	0.76
1	1	19.80	0.00	26	20.32	4.25	17	21.99	3.02	1	21.80	0.00	8	20.20	4.07	9	22.04	1.26
2	1	1.80	0.00	25	3.17	4.21	17	3.23	5.99	1	2.77	0.00	8	4.26	4.28	9	1.74	0.22
3	1	6.90	0.00	25	7.62	4.15	17	7.07	3.13	1	7.42	0.00	8	8.66	3.73	9	6.67	0.27
4	1	16.50	0.00	25	17.39	2.61	17	16.13	3.73	1	24.82	0.00	8	18.47	3.07	9	16.64	1.07
5	1	26.60	0.00	25	25.95	2.47	17	25.69	2.01	1	50.28	0.00	8	28.40	2.05	9	26.34	1.69

*Outliers removed.

TABLE 22. PERCENT OF SULFATE MEASUREMENTS WITHIN INDICATED PERCENT OF REFERENCE VALUE

Survey 0280						Survey 0880					
Sample no.	Reference value	10%	20%	30%	50%	Sample no.	Reference value	10%	20%	30%	50%
1	25.20	59.6	94.7	98.2	100.0	1	11.80	62.3	83.6	86.9	93.4
2	7.50	54.4	82.5	87.7	96.5	2	22.00	78.1	87.5	92.2	100.0
3	1.20	22.2	33.3	44.4	64.8	3	1.60	32.2	42.4	47.5	66.1
4	12.00	66.7	94.7	100.0	100.0	4	6.80	50.8	68.3	82.5	90.5
5	18.00	71.4	83.9	91.1	94.6	5	17.00	70.3	79.7	84.4	98.4
6	32.40	46.6	81.0	89.7	100.0	6	27.20	74.6	90.5	96.8	100.0

The means from sulfate survey 0280, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 1.0120 + 0.8615 (reference value)

$R^2 = 0.9986$

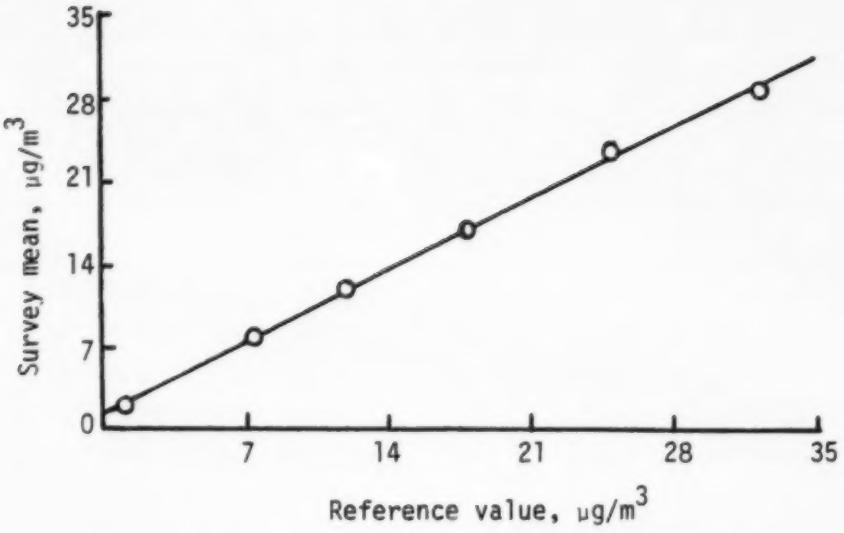
A plot of the survey 0280 means (y) against the reference values (x) is shown in Figure 9.

The mean values from survey 0880, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 0.8944 + 0.9348 (reference value)

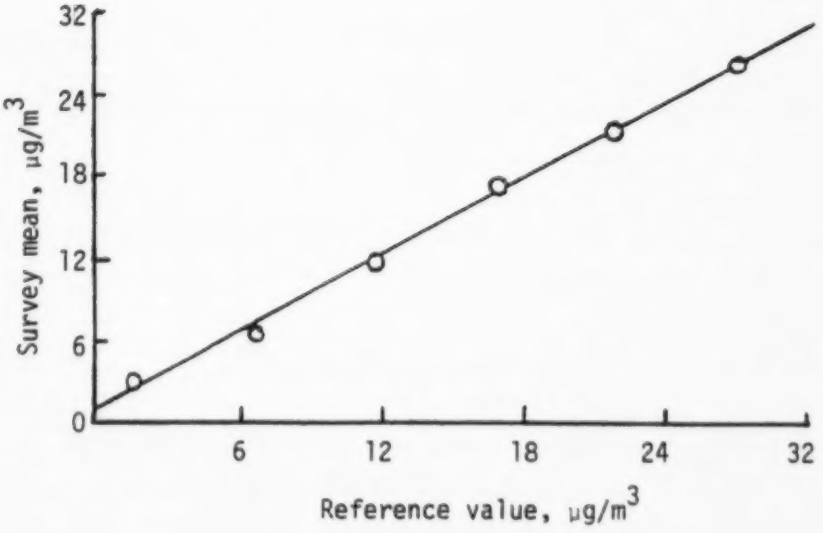
$R^2 = 0.9974$

A plot of the survey means (y) against the reference values (x) is shown in Figure 10.



x	y
1.20	1.81
7.50	7.50
12.00	11.45
18.00	16.58
25.20	23.24
32.40	28.45

Figure 9. Mean value of $SO_4^=$ survey 0280 vs. reference values.



x	y
1.60	2.92
6.80	6.52
11.80	11.72
17.00	17.21
22.00	21.49
27.20	26.27

Figure 10. Mean values of $SO_4^=$ survey 0880 vs. reference values.

Resume

Proficiency Surveys for $SO_4^=$ were conducted in February and August 1980. Approximately 60 laboratories participated. State and local agencies together composed about 72 percent of the participants. Six test methods were employed; the automated methylthymol blue and the manual barium chloride procedures dominated. Other major methods used were Sulfa-Ver© and ion chromatography.

NITRATE

Test Method

Approximately half of the respondents reported using the automated cadmium reduction method. The second most common method was ion chromatography. The balance of respondents used one of five other methods: phenoldisulfonic acid, brucine, specific ion electrode, Szechrome© and ultraviolet spectrophotometry.

The averages of the two principal test methods (automated cadmium reduction and ion chromatography) were compared by the t test. The difference between the means was without statistical significance. Generally, the precision of the ion chromatography method was superior. Application of the F test to the survey data demonstrated that the variability of the cadmium reduction method generally exceeded that of the ion chromatography in these surveys.

Agency Apportionment

Involvement of state agencies and industrial facilities in the nitrate surveys did not change noticeably from the previous survey year[7] though the number of local boards decreased somewhat. State and local offices embodied 62 percent of the total participation. The composition of the surveys is shown in Table 23.

TABLE 23. AGENCY APPORTIONMENT OF NITRATE SURVEYS

Agency	Survey 0280, %	Survey 0880, %
Federal	2	2
State	48	48
Local	14	14
Industrial/Contractor	26	26
Foreign	10	10

Data Summary

The survey results listed in Table 24 include all methods. Results by analytical method are given in Table 25. Frequency distributions by percent are shown in Table 26. The reference values used in the nitrate surveys were derived from the theoretical amounts of nitrate ion which were deposited on glass fiber filter strips. Confirmation analyses of the theoretical concentrations were accomplished by the QAD/EMSL, Stewart Laboratories, Inc., and by the manufacturer, Northrop Services, Inc.

TABLE 24. SUMMARY OF NITRATE PROFICIENCY SURVEYS

Sample no.	Respondents*	Reference value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0280 (February 1980)					
0	40	9.90	9.24	0.78	7.20 - 10.80
1	40	2.40	2.43	0.42	1.41 - 3.83
2	40	4.20	4.03	0.47	2.44 - 5.03
3	40	6.00	5.76	0.61	3.92 - 7.26
4	40	7.80	7.34	1.03	2.81 - 8.60
5	41	0.80	1.26	1.12	0.70 - 7.56
Survey 0880 (August 1980)					
0	42	6.00	5.84	0.66	3.48 - 7.65
1	42	11.40	11.25	0.71	10.00 - 13.80
2	42	0.60	0.86	0.52	0.30 - 2.91
3	42	3.30	3.32	0.39	2.66 - 4.77
4	44	8.70	8.52	0.94	5.99 - 11.20
5	43	14.10	13.26	1.41	8.40 - 14.88

*With outliers removed.

TABLE 25. NITRATE BY ANALYTICAL METHOD
($\mu g/m^3$)

	Cadmium reduction-manual			Cadmium reduction-automated			Ion chromatograph			Hydrazine reduction-automated			Hydrazine reduction-manual		
Sample no.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
Survey 0280* (February 1980)															
0	4	10.33	2.15	19	8.95	1.16	10	9.31	0.94	4	9.46	0.19	0		
1	4	2.83	0.70	19	2.62	1.29	10	2.28	0.18	4	2.60	0.60	0		
2	4	4.57	1.90	18	3.96	0.50	10	4.01	0.29	4	4.16	0.44	0		
3	4	6.01	0.94	18	5.60	0.67	10	5.56	0.87	4	6.16	0.45	0		
4	4	7.86	0.43	19	6.33	2.32	10	7.38	0.64	4	7.62	0.43	0		
5	4	1.29	0.45	19	1.39	1.53	10	0.89	0.15	4	1.55	1.27	0		
Survey 0880* (August 1980)															
0	3	4.28	2.78	21	5.18	1.44	9	5.76	0.49	5	6.17	0.72	2	6.50	2.83
1	3	12.10	0.61	22	10.29	2.32	9	11.32	1.02	5	11.10	0.62	2	9.86	5.04
2	3	0.62	0.33	22	1.08	1.53	9	0.67	0.19	5	0.79	0.64	2	1.56	1.05
3	3	2.55	1.52	22	3.17	0.99	9	3.18	0.14	5	3.69	0.63	2	4.21	1.29
4	3	8.38	0.55	22	8.50	2.20	9	8.62	1.07	5	8.84	0.41	2	9.32	4.28
5	3	14.01	1.07	22	12.60	2.99	9	13.88	0.54	5	13.40	1.36	2	13.66	4.46

*With outliers removed.

TABLE 26. PERCENT OF NITRATE MEASUREMENTS WITHIN INDICATED PERCENT OF REFERENCE VALUE

Survey 0280						Survey 0880					
Sample no.	Reference value	10%	20%	30%	50%	Sample no.	Reference value	10%	20%	30%	50%
1	9.90	66.7	82.2	88.9	93.3	1	6.00	73.3	84.4	91.1	97.8
2	2.40	51.1	75.6	82.2	86.7	2	11.40	80.9	89.4	91.5	97.9
3	4.20	68.2	84.1	88.6	90.9	3	0.60	44.4	55.6	60.0	73.3
4	6.00	63.6	81.8	88.6	93.2	4	3.30	78.3	82.6	87.0	93.5
5	7.80	62.2	80.0	84.4	86.7	5	8.70	74.5	85.1	91.5	100.0
6	0.80	34.1	45.5	54.5	68.2	6	14.10	76.6	85.1	91.5	100.0

The mean values from survey 0280, plotted against the reference values, gave a linear relationship, as follows:

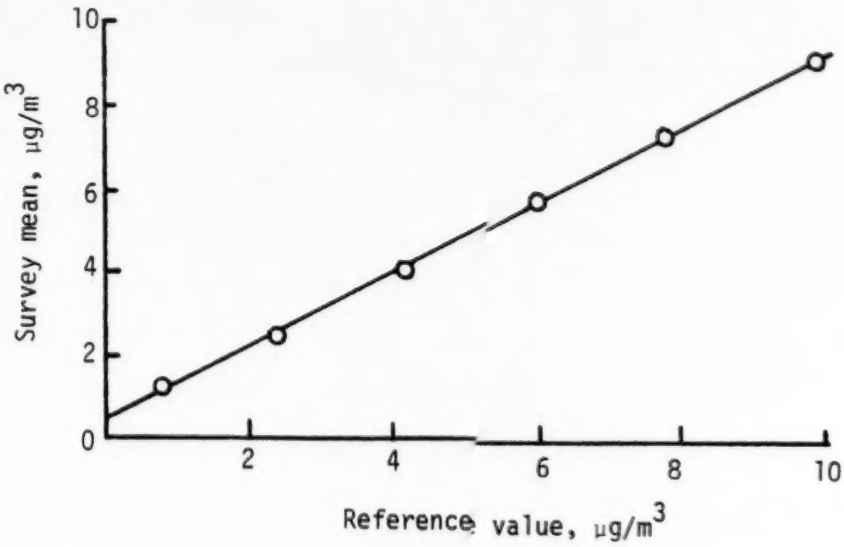
Survey average = 0.4058 + 0.8883 (reference value)
R^2 = 0.9990

A plot of the survey means (y) against the reference values (x) is shown in Figure 11.

The mean values from survey 0880, plotted against the reference values, gave a linear relationship, as follows:

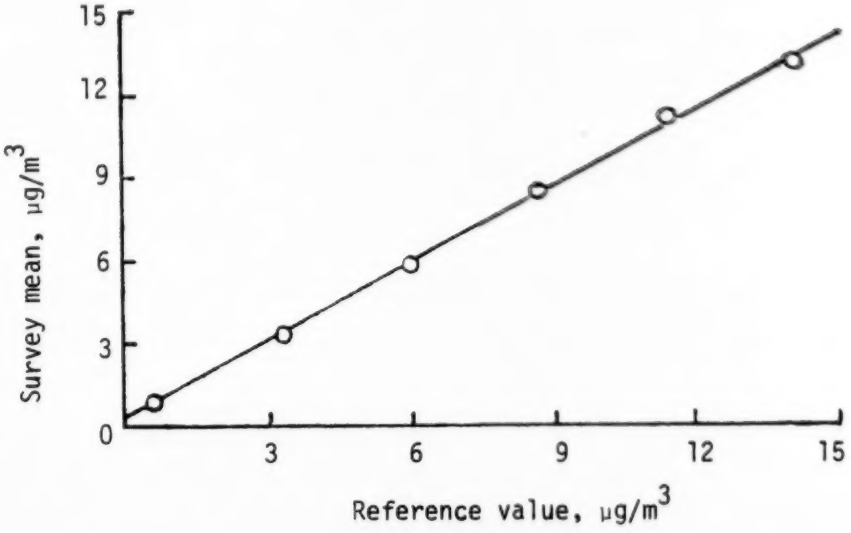
Survey average = 0.2940 + 0.9362 (reference value)
R^2 = 0.9987

A plot of the survey means (y) against the reference values (x) is shown in Figure 12.



x	y
0.80	1.26
2.40	2.43
4.20	4.03
6.00	5.76
7.80	7.34
9.90	9.24

Figure 11. Mean values of NO_3^- survey 0280 vs. reference values.



x	y
0.60	0.86
3.30	3.32
6.00	5.84
8.70	8.52
11.40	11.25
14.10	13.26

Figure 12. Mean values of NO_3^- survey 0880 vs. reference values.

Resume

Proficiency Surveys for NO_3^- were completed by approximately 40 participants in February and August, 1980. The predominant test method was the automated cadmium reduction procedure, used by about half the respondents. In all, seven analytical methods were reported. No method was particularly bad and no systematic discrepancies existed.

LEAD

Test Method

Virtually all participants in both the 0180 and 0780 surveys employed the atomic absorption analytical method as in previous years. One laboratory used the X-ray fluorescence method.

Agency Apportionment

In 1980, the number of industrial facilities participating in the lead surveys continued to increase. Those laboratories now constitute about 25 percent of the lead survey program. Participation by local agencies decreased somewhat from the previous survey year[7]. Agencies which were involved in the lead surveys are listed in Table 27.

TABLE 27. AGENCY APPORTIONMENT OF LEAD SURVEYS

Agency	Survey 0180, %	Survey 0780, %
Federal	6	5
State	49	47
Local	16	24
Industrial/Contractor	27	22
Foreign	2	2

Data Summary

The survey results are tabulated in Table 28, and results by analytical method are summarized in Table 29. Frequency distributions of the percent of the reference value are shown in Table 30. The reference values used in the lead surveys were designated after considering the theoretical values and the results of corroborative analyses by Stewart Laboratories, Inc. and those of the manufacturer of the samples, Northrop Services, Inc.

TABLE 28. SUMMARY OF LEAD PROFICIENCY SURVEYS

Sample no.	Respondents*	Reference value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0180 (January 1980)					
0	82	9.90	9.66	0.44	8.43 - 10.80
1	82	6.30	6.18	0.32	4.80 - 6.96
2	82	8.10	7.89	0.38	6.72 - 9.00
3	81	4.50	4.38	0.21	3.60 - 4.90
4	82	2.70	2.71	0.13	2.37 - 3.06
5	82	0.90	0.90	0.06	0.62 - 1.08
Survey 0780 (July 1980)					
0	81	0.60	0.58	0.04	0.45 - 0.67
1	82	6.60	6.51	0.35	5.30 - 7.44
2	81	1.80	1.80	0.13	1.39 - 2.16
3	83	5.40	5.34	0.36	3.91 - 6.42
4	82	3.00	2.99	0.16	2.47 - 3.30
5	84	4.20	4.10	0.21	3.56 - 4.64

*With outliers removed.

TABLE 29. LEAD BY ANALYTICAL METHOD
($\mu g/m^3$)

Sample no.	Atomic absorption			X-ray fluorescence		
	N	Mean	Std. dev.	N	Mean	Std. dev.
Survey 0180* (January 1980)						
0	82	9.66	0.44	0		
1	82	6.18	0.32	0		
2	82	7.89	0.38	0		
3	81	4.38	0.21	0		
4	82	2.71	0.13	0		
5	82	0.90	0.06	0		
Survey 0780* (July 1980)						
0	81	0.58	0.04	1	0.60	0.00
1	82	6.51	0.35	1	6.23	0.00
2	81	1.80	0.13	1	1.55	0.00
3	83	5.34	0.36	1	5.02	0.00
4	82	2.99	0.16	1	2.67	0.00
5	83	4.10	0.21	1	3.77	0.00

*Outliers removed.

TABLE 30. PERCENT OF LEAD MEASUREMENTS WITHIN INDICATED PERCENT OF REFERENCE VALUE

Survey 0180						Survey 0780					
Sample no.	Reference value	10%	20%	30%	50%	Sample no.	Reference value	10%	20%	30%	50%
1	9.90	85.6	92.2	92.2	94.4	1	0.60	85.9	94.1	100.0	100.0
2	6.30	83.3	91.1	94.4	95.6	2	6.60	87.2	98.8	100.0	100.0
3	8.10	85.4	93.3	94.4	97.8	3	1.80	80.0	95.3	100.0	100.0
4	4.50	83.3	90.0	92.2	94.4	4	5.40	86.0	98.8	100.0	100.0
5	2.70	84.4	91.1	93.3	95.6	5	3.00	90.7	97.7	100.0	100.0
6	0.90	85.1	93.1	94.3	96.6	6	4.20	87.2	100.0	100.0	100.0

The mean values from survey 0180, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 0.0461 + 0.9705 (reference values)
R^2 = 0.9999

A plot of the survey means (y) against the reference values (x) is shown in Figure 13.

The mean values from survey 0780, plotted against the reference values, gave a linear relationship, as follows:

Survey average = 0.0065 + 0.9852 (reference value)
R^2 = 0.9999

A plot of the survey 0780 means (y) against the reference values (x) is shown in Figure 14.

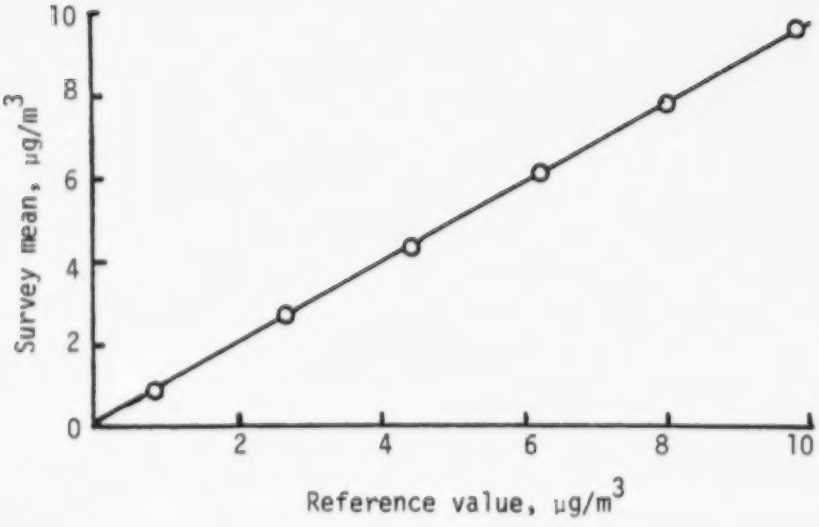
Resume

Proficiency Surveys for Pb were conducted in January and July 1980, with approximately 80 facilities participating. The atomic absorption method of analysis predominated.

HI-VOL FLOW

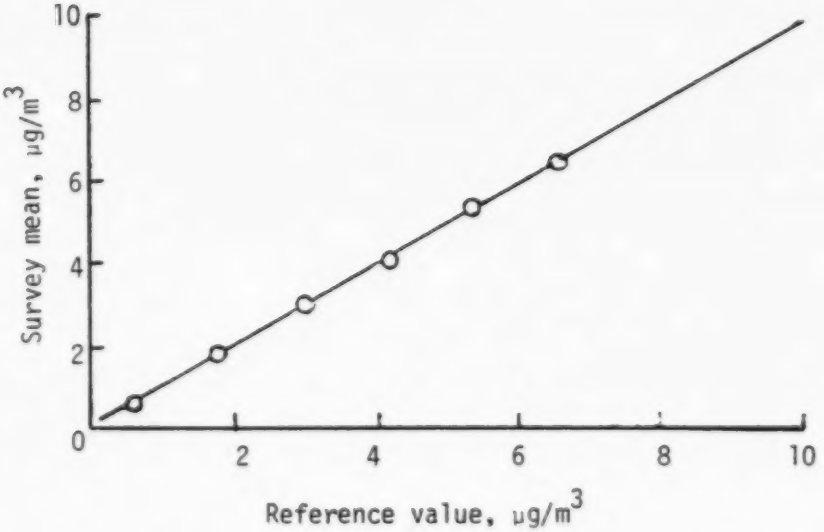
Test Method

Eight measurement methods were listed by survey participants. The pressure transducer (continuous) and rotameter dominated with 78 percent using those methods. Other minor methods, as noted on the survey information forms, were flow gauge, manometer, orifice manometer, flow controller and non-continuous pressure transducer. Five percent of the methodologies were indeterminate. The categories of various methods, together with a summary of sites are presented in Table 31.



x	y
0.90	0.90
2.70	2.71
4.50	4.38
6.30	6.18
8.10	7.89
9.90	9.66

Figure 13. Mean values of Pb survey 0180 vs. reference values.



x	y
0.60	0.58
1.80	1.80
3.00	2.99
4.20	4.10
5.40	5.34
6.60	6.51

Figure 14. Means of Pb survey 0780 vs. reference values.

TABLE 31. ANALYTICAL METHODS - HIGH-VOLUME FLOW

Method	No. of sites
Pressure transducer - flow controller	66
Flow controller	76
Rotameter	552
Pressure transducer - continuous recording	592
Flow gauge	17
Pressure transducer - non-continuous	18
Manometer	26
Orifice manometer	46
Other	43

Agency Apportionment

The number of air monitoring offices taking part in the 0580 survey increased by approximately 9 percent from the previous survey year[7]. Enlarged industrial participation principally accounted for the increase. The division of agencies is shown in Table 32.

TABLE 32. AGENCY APPORTIONMENT OF HIGH-VOLUME FLOW SURVEY

Agency	Survey 0580, %
Federal	0.4
State	37.5
Local	51.9
Industrial/Contractor	7.2
Foreign	3.0

Data Summary

It was not practical to furnish standardized ReF specimens from an invariant population of samples. Each sample ReF unit was calibrated individually and is distinct from all other units in as much as flow rates could not be duplicated precisely enough among the test devices to establish flow values that were applicable to all units. Rather than comparing collective measurements against a common standard, results from each ReF were compared to a calibration which is unique for that unit. The calibrated flow values, or reference values, developed for each of five flow constrictor plates, were compared to the values recorded on the survey forms. To facilitate the comparison, the reference values were termed "x" and the reported values "y". The five x, y pairs were plotted to obtain a linear regression plot, with the expectation that the coefficient of linearity (r) should be 1, the slope should be 1, and the y intercept should be zero. Departures from this norm are due to any single or combination of defects that falsify the measured flow. As described in Table 33, five categories of measurements were evaluated. The linear regression equations of the five categories are also given in Table 33. Table 31 makes reference to the secondary methods used in the survey.

TABLE 33. LINEAR REGRESSION EQUATIONS OF PAIRED HIGH-VOLUME VALUES

All Methods:	$y = 0.912x + 3.552$	(9)
Pressure transducer (continuous):	$y = 0.933x + 2.411$	(10)
Rotameter:	$y = 0.888x + 4.844$	(11)
Pressure transducer (flow controller):	$y = 0.939x + 1.501$	(12)
Flow gauge:	$y = 0.923x + 3.667$	(13)

where: y = reported value, cu. ft./min.
x = reference value, cu. ft./min.

Frequency distributions of the absolute percent differences from the reported and reference values for measurement pairs are shown in Table 34. The summary includes the two major measurement methods and the aggregate of reported values.

TABLE 34. ABSOLUTE PERCENT DIFFERENCE OF HIGH-VOLUME MEASUREMENTS FROM REFERENCE FLOW

Method(s)	Number of Measurements*	Percent of measurements				
		10	30	50	70	90
All	6390	0.61	1.93	3.62	6.20	11.33
Rotameter	2388	0.56	1.79	3.26	5.58	10.77
Pressure transducer (continuous)	2815	0.68	2.20	4.20	6.77	11.49

*With outliers removed.

Resume

The Proficiency Survey for hi-vol flow was conducted in May 1980 with approximately 1,436 sites being tested. Foreign, federal, state and industrial laboratories participated in the testing program. The pressure transducer and rotameter were the most common methods used; the four other methods were minor. A slight bias existed in the major methods and in the data from all methods combined.

SECTION 6
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*USGPO: 1982 — 659-095/0544